CURABLE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] Curable compositions, such as benzoxazine-based ones, are useful in applications within the aerospace industry, such as for example as a heat curable composition for use as a matrix resin or an adhesive, and form the basis of the present invention.

Brief Description of Related Technology

[0002] Epoxy resins with various hardeners have been used extensively in the aerospace and electronics industries both as adhesives and as matrix resins for use in prepreg assembly with a variety of substrates.

[0003] Benzoxazines themselves have been reported in the literature as generally having a high glass transition temperature, good electrical properties (e.g., dielectric constant), and low flammability.

[0004] Blends of epoxy resins and benzoxazines are known. See e.g. U.S. Patent Nos. 4,607,091 (Schreiber), 5,021,484 (Schreiber), 5,200,452 (Schreiber), and 5,445,911 (Schreiber). These blends appear to be potentially useful in the electronics industry, as the epoxy resins can reduce the melt viscosity of benzoxazines allowing for the use of higher filler loading while maintaining a processable viscosity. However, epoxy resins oftentimes undesirably increase the temperature at which benzoxazines polymerize.

[0005] Ternary blends of epoxy resins, benzoxazine and phenolic resins are also known. See U.S. Patent No. 6,207,786 (Ishida), and S. Rimdusit and H. Ishida, "Development of new class of electronic packaging materials based on ternary system of benzoxazine, epoxy, and phenolic resin," Polymer, 41, 7941-49 (2000).

[0006] Other resins, such as reactive monomers, polymers and oxazolines, polyimide/siloxane co-polymers and cyanate esters, are too known. See e.g. U.S. Patent No. 4,806,267 (Culbertson), in connection with oxazolines and J. McGrath et al., "Synthesis and Characterization of Segmented Polyimide-Polyorganosiloxane Copolymers", Advances in Polym. Sci., Vol. 140, Springer-Verlag, Berlin 61-105 (1999) in connection with polybenzoxazine polyimide-polyorganosiloxane co-polymers.

[0007] Moreover, in J. Jang et al., "Performance Improvement of Rubber Modified Polybenzoxazine", J. Appl. Polym. Sci., 67, 1-10 (1998), the authors report the use of polybenzoxazine modified with amine-terminated, butadiene acrylonitrile rubber

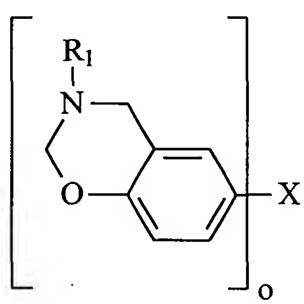
and with carboxyl-terminated, butadiene acrylonitrile rubber to improve mechanical properties. The polybenzoxazine chosen was synthesized from bisphenol A, formaldehyde and the aromatic amine, aniline.

[0008] Notwithstanding the state of the technology, there has been no disclosure, teaching or suggestion to prepare a heat curable composition based on the combination of a benzoxazine prepared from bisphenol A, formaldehyde and alkyl amines, and amine-terminated, butadiene acrylonitrile rubber, let alone one with improved performance properties.

SUMMARY OF THE INVENTION

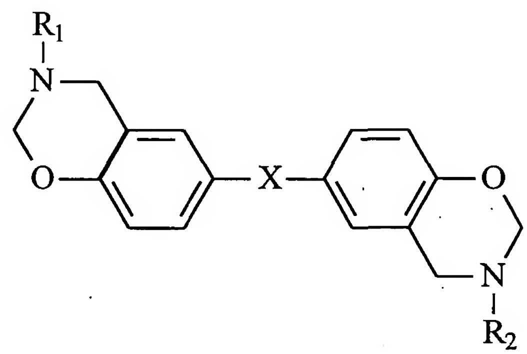
[0009] The inventive compositions include a heat curable composition comprising the combination of a benzoxazine component and a toughener component.

[0010] In one aspect, the invention provides a benzoxazine component comprising



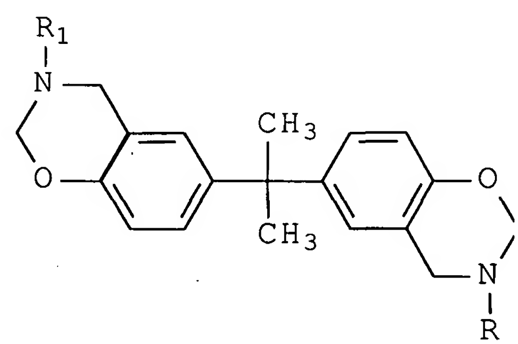
where o is 1-4, X is a direct bond (when o is 2), alkyl (when o is 1), alkylene (when o is 2-4), carbonyl (when o is 2), thiol (when o is 1), thioether (when o is 2), sulfoxide (when o is 2), and sulfone (when o is 2), and R_1 is alkyl, such as methyl, ethyl, propyls and butyls; and a toughener component comprising acrylonitrile-butadiene co-polymer having secondary amine terminal groups ("ATBN").

[0011] In a more specific embodiment of that aspect of the invention, the benzoxazine component is embraced by



where X is selected from the group consisting of a direct bond, CH_2, $C(CH_3)_2$, C=O, S, S=O and O=S=O, and R_1 and R_2 are the same or different and are selected from methyl, ethyl, propyls and butyls.

[0012] In yet a more specific embodiment of that aspect of the invention, the benzoxazine component is embraced by



where R_1 and R_2 are the same or different and are selected from methyl, ethyl, propyls and butyls, though in a particularly desirable embodiment R_1 and R_2 are each methyl.

[0013] Cured reaction products of the inventive compositions are capable of demonstrating at least one of a wet Tg of at least 350 °F, such as in the range of 350 to 450°F, a toughness measured by G_{Ic} of at least 1.9 in-lb./in^2, such as in the range of 1.9 to 4.0 in-lb./in^2, a percent decrease in ΔH of at least

15% compared with a benzoxazine prepared from bisphenol F and aniline, and a percent decrease in wet Tg compared with dry Tg with increased toughener concentration of less than 6%.

[0014] Cured reaction products of the inventive compositions are also capable of demonstrating a Tg and toughness measured by GI_c increase as the amount of toughener in the composition increases.

[0015] Moreover, cured reaction products of the inventive compositions should also have a cured density of less than 1.2 g/cc.

[0016] The invention is further directed to prepregs of the inventive compositions and cured reaction products thereof, prepregs of the inventive compositions and cured reaction products thereof, towpregs of the inventive compositions and cured reaction products thereof, and processes for producing the prepregs and towpregs, adhesive compositions of the inventive compositions and films thereof, methods of preparing and using the inventive compositions, articles of manufacture assembled with the inventive compositions and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Figure 1 depicts a plot of glass transition temperature (left y axis) vs. toughness vs. G_{IC} (right y axis) for benzoxazine with increasing ATBN concentration.

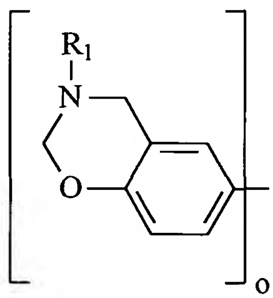
[0018] Figure 2 is a representation of Figure 3 from J. Jay et al., depicting a plot of G_{IC} vs. ATBN and acrylonitrile-butadiene co-polymer having carboxyl terminal groups ("CTBN") concentration.

[0019] Figure 3 is a representation of Figure 6 from J. Jay, et al., depicting a plot of Tg vs. ATBN and CTBN concentration.

DETAILED DESCRIPTION OF THE INVENTION

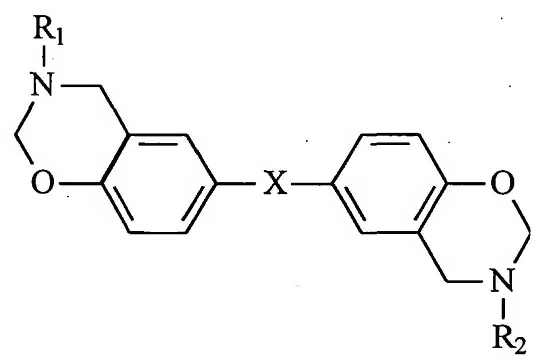
[0020] As noted above, the present invention provides generally a heat curable composition comprising the combination of a benzoxazine component and a toughener component.

[0021] In one aspect, the invention provides a benzoxazine component comprising



where o is 1-4, X is a direct bond (when o is 2), alkyl (when o is 1), alkylene (when o is 2-4), carbonyl (when o is 2), thiol (when o is 1), thioether (when o is 2), sulfoxide (when o is 2), and sulfone (when o is 2), and R_1 is alkyl, such as methyl, ethyl, propyls and butyls; and a toughener component comprising ATBN.

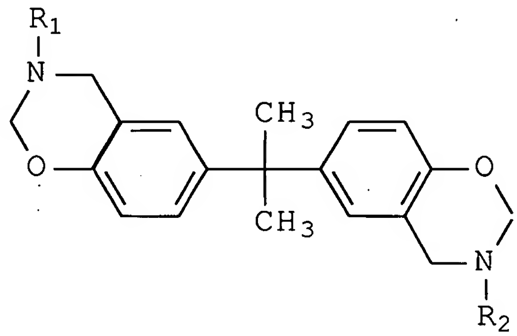
[0022] In a more specific embodiment of that aspect of the invention, the benzoxazine component is embraced by



where X is selected from the group consisting of a direct bond, CH_2, $C(CH_3)_2$, C=O, S=O and O=S=O, S, and R_1 and R_2 are the same or

different and are selected from methyl, ethyl, propyls and butyls.

[0023] In yet a more specific embodiment of that aspect of the invention, the benzoxazine component is embraced by



where R_1 and R_2 are the same or different and are selected from methyl, ethyl, propyls and butyls, though in a particularly desirable embodiment R_1 and R_2 are each methyl.

[0024] Cured reaction products of the inventive compositions are capable of demonstrating at least one of a wet Tg of at least 350 °F, such as in the range of 350 to 450°F, a toughness measured by G_{Ic} of at least 1.9 in-lb./in^2, such as in the range of 1.9 to 4.0 in-lb./in^2, a percent decrease in ΔH of at least 15% compared with a benzoxazine prepared from bisphenol F and aniline, and a percent decrease in wet Tg compared with dry Tg with increased toughener concentration of less than 6%.

[0025] Cured reaction products of the inventive compositions are also capable of demonstrating improved Tg and toughness measured by GI_c increase as the amount of toughener in the composition increases.

[0026] Moreover, cured reaction products of the inventive compositions should also have a cured density of less than 1.2 g/cc.

[0027] The benzoxazine component should be present in an amount in the range of about 10 to about 99 percent by weight, such as about 25 to about 75 percent by weight, desirably about

35 to about 65 percent by weight, based on the total weight of the composition.

[0028] The toughener component, ATBN, should be present in an amount in the range of about 1 to about 90 percent by weight, such as about 10 to about 70 percent by weight, desirably about 15 to about 30 percent by weight, based on the total weight of the composition.

[0029] The benzoxazine component of the present invention may typically be prepared by reacting a phenolic compound, such as a bisphenol A, bisphenol F, bisphenol S or thiodiphenol, with an aldehyde and an alkyl amine. U.S. Patent No. 5,543,516, hereby expressly incorporated herein by reference, describes a method of forming benzoxazines, where the reaction time can vary from a few minutes to a few hours, depending on reactant concentration, reactivity and temperature. <u>See also</u> Burke et al., <u>J. Org. Chem.</u>, 30(10), 3423 (1965); <u>see generally</u> U.S. Patent Nos. 4,607,091 (Schreiber), 5,021,484 (Schreiber), 5,200,452 (Schreiber) and 5,443,911 (Schreiber).

[0030] Benzoxazines are presently available from several sources commercially, including Vantico, Inc., Brewster, New York, Georgia-Pacific Resins, Inc. and Shikoku Chemicals Corporation, Chiba, Japan, the least of which offers among others B-a, B-m, F-a, C-a and F-a benzoxazine resins. Of these, the benzoxazine component of the present invention is oftentimes desirably within the B-m benzoxazine resin family.

[0031] Benzoxazine polymerization can also be initiated by cationic initiators, such as Lewis acids, and other known cationic initiators, such as metal halides; organometallic derivatives; metallophorphyrin compounds such as aluminum phthalocyanine chloride; methyl tosylate, methyl triflate, and triflic acid; and oxyhalides.

[0032] The inventive compositions may also include coreactants, curatives and/or catalysts for the benzoxazines component. Examples include Lewis acids, such as phenols and derivatives thereof, strong acids, such as alkylenic acids and cationic catalysts.

[0033] The invention relates also to prepregs formed from a layer of fibers infused with the inventive heat curable composition.

[0034] In this regard, the invention relates also to a processes for producing a prepreg. One such process includes the steps of (a) providing a layer of fibers; (b) providing the inventive heat curable composition; and (c) joining the heat curable composition and the layer of fibers to form a prepreg assembly, and exposing the resulting prepreg assembly to elevated temperature and pressure conditions sufficient to infuse the layer of fibers with the heat curable composition to form a prepreg.

[0035] Another such process for producing a prepreg, includes the steps of (a) providing a layer of fibers; (b) providing the inventive heat curable composition in liquid form; (c) passing the layer of fibers through the liquid heat curable composition to infuse the layer of fibers with the heat curable composition; and (d) removing excess heat curable composition from the prepreg assembly.

[0036] The fiber layer may be constructed from unidirectional fibers, woven fibers, chopped fibers, non-woven fibers or long, discontinuous fibers.

[0037] The fiber chosen may be selected from carbon, glass, aramid, boron, polyalkylene, quartz, polybenzimidazole, polyetheretherketone, polyphenylene sulfide, poly p-phenylene benzobisoaxazole, silicon carbide, phenolformaldehyde, phthalate and napthenoate.

[0038] The carbon is selected from polyacrylonitrile, pitch and acrylic, and the glass is selected from S glass, S2 glass, E glass, R glass, A glass, AR glass, C glass, D glass, ECR glass, glass filament, staple glass, T glass and zirconium oxide glass.

[0039] The invention further contemplates a towpreg formed from a bundle of such fibers infused with the inventive heat curable composition.

[0040] In this regard, the invention relates also to processes for producing a towpreg. In one such process, the steps include (a) providing a bundle of fibers; (b) providing the heat curable composition and (c) joining the heat curable composition and the bundle of fibers to form a towpreg assembly, and exposing the resulting towpreg assembly to elevated temperature and pressure conditions sufficient to impregnate the bundle of fibers with the heat curable composition to form a towpreg.

[0041] In another such process, the steps include (a) providing a bundle of fibers; (b) providing the inventive heat curable composition in liquid form; (c) passing the bundle of fibers through the liquid heat curable composition to impregnate the bundle of fibers with the heat curable composition; and (d) removing excess heat curable composition from the towpreg assembly, thereby forming the towpreg.

[0042] The inventive composition may also include an additional toughener component, examples of which include poly(propylene) oxide; amine-terminated polyethylene sulfide, such as PES 5003P, available commercially from Sumitomo Chemical Company, Japan; core shell polymers, such as PS 1700, available commercially from Union Carbide Corpoartion, Danbury, Connecticut; and BLENDEX 338, SILTEM STM 1500 and ULTEM 2000, which are available commercially from General Electric Company.

ULTEM 2000 (CAS Reg. No. 61128-46-9) is a polyetherimide having a molecular weight ("Mw") of about 30,000 ± 10,000.

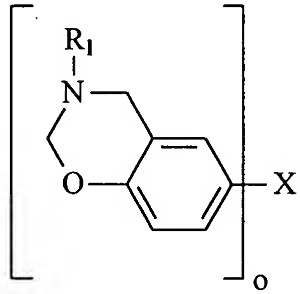
[0043] The inventive composition may be in the form of an adhesive, in which case one or more of an adhesion promoter, a flame retardant, a filler, a thermoplastic additive, a reactive or non-reactive diluent, and a thixotrope should be included. In addition, the inventive adhesive may be placed in film form, in which case a support constructed from nylon, glass, carbon, polyester, polyalkylene, quartz, polybenzimidazole, polyetheretherketone, polyphenylene sulfide, poly p-phenylene benzobisoaxazole, silicon carbide, phenolformaldehyde, phthalate and napthenoate should be included.

[0044] Compositions of the present invention may ordinarily be cured by heating to a temperature in the range of about 120 to about 180°C for a period of time of about 30 minutes to 4 hours. Thus, the inventive compositions can be used at relatively moderate temperatures to achieve very good productivity.

[0045] The inventive compositions (and pregregs and towpregs prepared therefrom) are particularly useful in the manufacture and assembly of composite parts for aerospace and industrial end uses, bonding of composite and metal parts, core and core-fill for sandwich structures and composite surfacing.

[0046] The invention also provides a process for producing a heat curable composition. The steps of this process includes:

(a) providing a benzoxazine comprising



where o is 1-4, X is a direct bond (when o is 2), alkyl (when o is 1), alkylene (when o is 2-4), carbonyl (when o is 2), thiol (when O is 1), thioether (when o is 2), sulfoxide (when o is 2), sulfone (when O is 2) and R_1 is alkyl;

(b) providing with mixing a toughener component comprising acrylonitrile-butadiene co-polymer having secondary amine terminal groups; and

(c) mixing the benzoxazine and the toughener component under conditions appropriate to produce the heat curable composition.

[0047] This invention is further illustrated by the following representative examples.

EXAMPLES

[0048] In a first comparative example, the following components were used to prepare Sample Nos. 1-2 as noted in Table 1.

Table 1

Component	Sample No./ Amt. (parts)	
	1	2
Benzoxazine*	75	75
Epoxy**	25	25
ATBN	--	10

* believed to have been made from bisphenol F, thiodiphenol, aniline and formaldehyde, and is available from Vantico under trade designation RD 2001-081.
** CY179, commercially available from Vantico.

[0049] Each of the samples was prepared as follows:

[0050] The benzoxazine was warmed at a temperature in the range of 180-200°F to render it flowable, without initiating curing.

[0051] Where an epoxy component was present, the flowable benzoxazine was mixed with the epoxy at a temperature of 180°F until a homogeneous mixture was formed.

[0052] Where ATBN was present, the ATBN was mixed into the mixture at a temperature in the range of 160-180°F.

[0053] The composition so formed was mixed under a vacuum, at a temperature in the range of 160-180°F for a period of time of 15-30 minutes. The so formed composition was stored in a closed container at room temperature.

[0054] The samples noted in Table 1 may be cured in an open face mold placed in an autoclave using the following cure profile:

[0055] The samples were exposed to 90 psi pressure within the autoclave and the temperature therein was increased at a 5°F/min ramp rate to a temperature of 350°F, for a period of time of about 3 hours. The cured samples were then cooled to a temperature of about 90°F in the mold at a 5°F/min ramp rate for a period of time of about 1 hour before use or evaluation.

[0056] The cured samples were evaluated using the following property tests:

[0057] Dynamic mechanical thermal analysis ("DMTA") was performed on cured samples using a double cantilever fixture. The cured samples were isothermally equilibrated at a temperature of 40°C in an oven and the temperature was increased at a 5°C/min ramp rate to a temperature of 250°C. Tg values were obtained from this DMTA evaluation from onset G′, storage shear modulus.

[0058] The cured samples were also subjected to boiling water for 3 days, and weight gain was recorded. Tg values were obtained from these samples using a DMTA evaluation.

[0059] Density of uncured and cured samples was measured according to ASTM D 792, and cure shrinkage was then calculated.

[0060] Flexure strength and modulus was determined in accordance with ASTM D 790, using cured samples with the following specimen dimensions: 0.125 x 0.5 x 4 in., span 2 in., test speed: 0.05 in./min.

[0061] K_{IC} and G_{IC} was determined in accordance with ASTM D5045-96, using single edge notch bending ("SENB") specimens of the cured samples.

[0062] The results of these evaluations on Sample Nos. 1-2 are set forth in Table 2.

Table 2

Properties	**Sample No.**	
	1	**2**
Cured density	1.24	1.20
Cure shrinkage	--	-1.8
T_g, °C	192	190
Hot/Wet T_g, °C	158	159
Moisture uptake	1.8	2.1
Flexure strength	17	15
Flexure modulus	0.70	0.50
G_{IC}, in-lb./in^2	0.6	1.4

[0063] In comparing these results from Sample Nos. 1 and 2, it is clear that Tg did not change appreciably by the addition of ATBN in this benzoxazine-epoxy system. Also, fracture toughness in terms of G_{IC} increased over two fold. However, the comparison between Tg and Hot/Wet Tg of Sample Nos. 1-2 each had a large decrease. This is undesirable because under service conditions, a finished part made with such a composition would experience a low service temperature.

[0064] Next, Sample Nos. 3-11, which are within the scope of the invention, were prepared using Bm-type benzoxazine and, where noted, ATBN in the amounts noted in Tables 3a and 3b. Sample No. 3, without ATBN, was used for comparative purposes.

Table 3a

Components	Sample No./ Amt. (parts)				
	3	4	5	6	7
B-m type Benzoxazine	100	95	90	85	80
ATBN	--	5	10	15	20

Table 3b

Components	Sample No./ Amt. (parts)			
	8	9	10	11
B-m type Benzoxazine	70	60	50	40
ATBN	30	40	50	60

[0065] The preparation process for each of Sample Nos. 3-11 was as described above with respect to Sample Nos. 1-2, as was the cure profile.

[0066] Sample Nos. 3-11 were cured and evaluated for property performance, results of which are shown below in Tables 4a and 4b.

Table 4a

Properties	Sample No.				
	3	4	5	6	7
ΔH, J/g	-213	-207	-173	-168	-154
Cured density		1.12		1.09	
Cure shrinkage				1.0	
T_g, °C	177	180	188	197	202
Hot/Wet T_g, °C	168	170	182	190	202
Moisture uptake	1.1	1.1	1.1	1.5	1.3
G_{IC}, in-lb./in^2	0.7	2.3	1.9	2.3	3.2

Table 4b

Properties	Sample No.			
	8	**9**	**10**	**11**
ΔH, J/g	-100	-76	-54	-45
Cured density	1.08	1.04	1.00	0.99
Cure shrinkage				
T_g, °C	204	204	227	232
Hot/Wet T_g, °C	208	217	222	232
Moisture uptake	1.1	1.4	1.7	2.2
G_{IC}, in-lb./in^2	4.0			

[0067] In comparing these results from Sample Nos. 3-11, it is clear that Tg increased with the addition of ATBN into the Bm-type benzoxazine. Also, fracture toughness in terms of G_{IC} increased with increased amounts of ATBN. And, the comparison between Tg and Hot/Wet Tg of Sample Nos. 3-11 showed that there was not an appreciable difference in these values, quite unlike the values observed with Sample Nos. 1-2.

[0068] For further comparative purposes, Sample Nos. 12-20 were prepared using either a bisphenol F-type, bisphenol A-type, Bm-type benzoxazine (as indicated) and, where noted, an epoxy resin, together with the tougheners incidated, ATBN in the amounts noted in Tables 5a and 5b.

Table 5a

Components		Sample No./ Amt. (parts)				
Type	Identity	**12**	**13**	**14**	**15**	**16**
Benzoxazine	B-m	--	--	--	--	--
	Bisphenol F	75	75	50	55	58
	Bisphenol A	--	--	--	--	--
Epoxy	CY 179	25	25	50	45	42
Toughener	ATBN	--	10	--	--	--
	SILTEM*	--	--	13	--	--
	PES 5003P**	--	--	--	9	17
	CTBN	--	--	--	--	--

Table 5b

Components		Sample No./ Amt. (parts)			
Type	Identity	17	18	19	20
Benzoxazine	B-m	--	--	100	100
	Bisphenol F	100	--	--	--
	Bisphenol A	--	80	--	--
Epoxy	CY 179	--	20	--	--
Toughener	ATBN	--	--	--	18
	SILTEM*	--	--	--	--
	PES 5003P**	--	--	--	--
	CTBN	10	--	--	--

* Co-polymer of ULTEM 2000 and siloxane

** Polyether sulfone, commercially available from Sumitomo

[0069] The preparation process for each of Sample Nos. 12-20 was as described above with respect to Sample Nos. 1 and 2, as was the cure profile.

[0070] Performance property evaluation of Sample Nos. 12-20 was performed as follows, with the results recorded in Tables 6a-6b.

[0071] Uncured samples were evaluated by Differential Scanning Calorimetry ("DSC"), within a temperature range of 40-350°C, where the temperature range increased at a 20°C/min ramp rate, and from which ΔH was recorded.

[0072] Cured samples were evaluated as above.

Table 6a

Property	Sample No.				
	12	13	14	15	16
ΔH, J/g	-367	-320	-340	-266	-263

Table 6b

Property	Sample No.			
	17	18	19	20
ΔH, J/g	-353	-431	-213	-168

[0073] Reference to Figures 1-3 shows that with the inventive composition (illustrated in Figure 1), an increase of ATBN concentration improves G_{IC} and dry Tg and Hot/Wet Tg, while with benzoxazines outside of the claimed structure (illustrated in Figures 2-3), an increase of ATBN concentration improves G_{IC} but decreases Tg. Figure 1 shows that in the inventive composition Tg and toughness measured by G_{Ic} increase as the amount of toughener in the composition increases, whereas Figures 2 and 3 show that with either an aryl substituted benzoxazine (that is, where R_1 and/or R_2) and/or CTBN instead of ATBN the opposite result is illustrated.

[0074] An increased Tg such as 200 (dry), together with increased toughness such as 3, are not ordinarily found in the same thermoset system. One known exception to this is Cytec Industries 977-2, which provides an epoxy prepeg thermoset. However, this Cytec product is known to have a moisture uptake of about 3 to 5%, which contributes to low Hot/Wet Tg (such as about 300), and a high ΔH, such as 500-700 J/g, compared to the inventive compositions, which are demonstrated to be lower than 500 J/g with one as low as 163 J/g. A lower ΔH is desirable so that stresses within the assembled structure are not caused during cooling. And the thermosets from the inventive compositions have the potential to reach an increased Tg ordinarily not found, unless insoluble toughener materials are added, or have an unacceptable viscosity for many commercial applications.